Two Refrigerant Mixtures and the Hard Sphere Fluid

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ABSTRACT

This is a discussion of the use of the perturbed hard sphere equation of state to describe refrigerants and refrigerant mixtures. A brief review of mixture modeling is given. Two mixtures, R13B1/R152a, and R12/R22, are discussed as examples of the usefulness of the model.

INTRODUCTION

The past decade has been witness to a surge of interest in the use of mixtures as working fluids in heat pump/refrigerating/airconditioning applications (Bougard, 1980) and in the geothermal power industry (Kestin et al. 1980). Anyone proposing to use a mixture is confronted with two questions: first, what are the properties of the mixture; and, second, are there effective ways of summarizing experimental information and predicting properties where there is no information? In this paper, we discuss the properties of two mixtures, the first, bromotrifluoromethane (R13B1) and 1,1-difluoroethane (R152a), a mixture without an azeotrope but whose properties deviate from the ideal mixing model, and the second, dichlorodifluoromethane (R12) and chlorodifluoromethane (R22), a mixture with an azeotrope.

The next and following sections of this paper discuss the physical foundation of the equation of state we have used to describe these mixtures, the perturbed hard sphere equation of state, and the problems associated with extending such an equation, originally intended for a pure fluid, to mixtures. Although the equation of state proposed here is different in fundamental ways from the traditionally used industrial equations, the problems connected to the notion of 'mixing rules' are universally applicable. In the later sections of this paper, comparisons are made between the measured properties of the mixtures and the properties correlated and predicted by the equation of state. The final section, before the concluding remarks, discusses some of the problems connected with critical points in the phase diagram.

THE EQUATION OF STATE

Let us briefly review the classes of equation of state and the conditions under which they apply. The simplest of all equations is the perfect gas law, $pv/RT = 1$. It is appropriate only for gases at very low pressures, less than 15 psia (0.10 MPa), and typically would be used only for making 'ballpark' calculations. There are a number of ways that the elegant form of this equation has been used to expand its range of usefulness; we shall consider two for which there are firm theoretical foundations. First is the virial equation of state (Mason and Spurling 1969), $pv/RT = 1 + B(T)/v +...$ When this equation is truncated at the second virial coefficient, $B(T)$, it is appropriate to pressures as high as 150 psia (1.0 MPa); however, only in the gas phase.

A second approach is the reduced equation of state, $pv/RT = f_1(T_r, v_r) + \omega f_2(T_r, v_r)$. The functions f_1 and f_2 are universal functions of the reduced temperature and volume based on experimental data (Edmister 1958) and the function, ω, the acentric factor, is an empirical

device to compensate for the nonspherical nature of molecules. This equation of state form, although rooted in a theoretical model, depends upon data for real materials to evaluate f_1 and f_2. Such equations of state are appropriate at all conditions and are limited by the knowledge of the reference fluids and the ability of ω to compensate for the shape of the molecule.

The van der Waals equations of state, $pv/RT = v/(v-b) + f(v,T)$, make up a large fraction of the equations used in industry. The first term compensates for the excluded volume during a bimolecular encounter. The second term accounts for the attraction between molecules; in addition, it is used to compensate for deficiencies in the first term. Such equations of state are quantitative only in the gas phase; they typically represent the liquid poorly. At high densities, the treatment of the excluded volume is both inadequate and incorrect (Henderson 1979).

Finally, there are equations of state founded on the properties of a theoretical reference fluid such as the Lennard-Jones fluid (Verlet and Levesque 1967) and the hard sphere fluid (Carnahan and Starling 1969). In a sense, this final approach is a theoretical response to the empirical reduced equation of state. The advantages to this last approach are at least two-fold: first, the packing problem at high densities is correctly addressed; second, the reference fluid itself is a well characterized material on which well controlled experiments can be performed. The equations arising from these models have the added advantage that their parameters have a direct physical interpretation.

In this paper, we are proposing to use a single equation of state to describe both the liquid and vapor phases of the pure materials and their mixtures. The approach taken here is to fashion the properties of the real fluid with respect to a reference fluid, in particular, the hard-sphere fluid as represented by the Carnahan-Starling equation of state (Carnahan and Starling 1969), which is modified by adding a term similar to the second term in the Redlich-Kwong equation of state (De Santis et al. 1976) as seen in Equation 1.

$$\frac{pv}{RT} = \frac{1 + y + y^2 - y^3}{(1 - y)^3} - \frac{a}{RT(v + b)} \quad ; \quad y = b/4v \tag{1}$$

In a mathematical sense, the second term gives rise to the liquid-vapor phase transition; in a physical sense, it is a consequence of the long-range attractive forces between the molecules. The thermodynamic functions that arise from this equation of state are listed in Appendix A. Of course for a complete description of the fluid, perfect gas heat capacities also need to be known. Although the heat capacities are available for the species examined in this paper, none of the calculations discussed here requires them.

The parameters, a and b, are determined by finding the values that not only satisfy the liquid-vapor equilibrium conditions but also best represent the known properties at saturation. The criterion for 'best described' is the values of a and b that minimize the function

$$F = \left(\frac{v_\ell - v_\ell(EOS)}{v_\ell}\right)^2 + \left(\frac{v_g - v_g(EOS)}{v_g}\right)^2 + \left(\frac{p - p(EOS)}{p}\right)^2 \tag{2}$$

Here v_ℓ and v_g, are the saturation liquid and vapor volumes respectively and p is the saturation pressure. Those quanties followed by '(EOS)' are the respective properties predicted at equilibrium by the equation of state. The parameters, a and b, are then fit to functions of temperature; details of the functional form and the values of the coefficients are found in Appendix B. The details of the procedures for finding the molecular parameters and locating the phase boundaries by the equation of state are found elsewhere (McLinden and Morrison 1985).

THE MIXING RULES

An important feature of any model is its ability to predict properties of a material when there are no data or, more correctly, when there are only remotely related data. For example, the method of corresponding states (Rowlinson and Swinton 1983a) coupled with critical point information and the value of the acentric factor (Pitzer 1955) allows one to guess the saturation properties of a pure material with considerable accuracy. Other schemes, such as the functional group contribution scheme (Ambrose 1978), allow one to make very good guesses about the properties of a material by knowing only its molecular structure. These techniques give the appearance that quantitative information can be generated from 'nothing.' Such models depend

The thesis on which the schemes described by Knobler and Pesuit are constructed is that the nature of the unlike interaction in a mixture can be estimated solely from the known like interactions. This thesis neglects the possibility that there can be interactions in a mixture that either do not occur or are unimportant in the pure materials. Recently, Gubbins and his colleagues have attempted to evaluate functions related to f_{12} from the multipole-multipole interactions between molecules (Gubbins and Twu 1978). In a recent paper Wallis et al. (1984) have shown that this approach can be used effectively in describing mixtures of CO_2 and ethane. In this paper, experimental information is used to evaluate the equation of state parameters connected to the mixtures.

EQUILIBRIUM PROPERTIES OF R13B1/R152a

In this section, we will describe the properties of a mixture that does not have an azeotrope, R13B1/R152a. Unlike most azeotropic refrigerant mixtures, there is little published information about this mixture. The first part of this section will be devoted to a brief description of the experiments conducted on this mixture and the nature of the data. (A more thorough discussion of these data will be made elsewhere (Morrison and Neal 1985).) We will then discuss the correlation of those data using the perturbed hard sphere equation of state.

Samples for this study were prepared by distilling measured quantities of each of the components from a gas buret into a stainless steel thermocompressor at liquid nitrogen temperature. The amount of each of the components was determined in two ways: first, an approximate determination by using the temperature-pressure-volume measurements from the gas buret and the values of the second virial coefficient predicted by the equation of state described earlier in this paper; second, by weighing the thermocompressor after each successive addition of the components (Morrison and Kincaid 1983). The second virial coefficient for R152a agreed within experimental uncertainty with the values listed by Dymond and Smith (1969); those values were derived from the measurements of Mears et al. (1955). Second virial coefficients for R13B1 were not available in the literature. The measurements included runs on each of the pure refrigerant materials and on mixtures that were roughly 25, 33, 50, 67, and 75 mole percent R152a. The mixtures were moved from the thermocompressor into the sample cell, which was constructed from a drawn sapphire tube and had a volume of approximately 0.43 in^3 (7.0 mL) (Davis 1983). The volume accessible to the sample could be changed, however, by raising and lowering the mercury level in the sapphire tube.

The cell was kept in a water bath whose temperature was controlled to +/- 0.0002 F (0.0003 K); the temperature was measured with a quartz crystal thermometer calibrated with an NBS-calibrated 25 Ohm platinum resistance thermometer. The total volume accessible to the sample and the volumes of the individual phases were determined to +/- 0.5% by measuring the distances between the top of the cell and the liquid-vapor meniscus or the liquid mercury meniscus. The volume of the cell was calibrated with triply distilled mercury. Pressures were measured to 0.15 psia (1 kPa) with a differential gauge calibrated with a dead-weight gauge.

Measurements of the liquid and vapor volumes and the pressure were made at five nearly equally spaced temperatures between 51 F (16°C) and 131 F (55 °C). Several sets of measurements were made by progressively enlarging the volume accessible to the sample. The results most immediately determined from these data are the liquid molar volume and the pressure on the bubble line. Although no samples of either phase were taken during the experiments, there is sufficient information in these data to locate the dew point curve (Knobler and Scott 1982). The data for the bubble curves are shown in Figures 1a and 1b; the solid and dashed lines are the correlated bubble loci and the predicted dew loci, respectively. The composition of the dew phase in equilbrium with the 50% mixture is shown. One should note the dramatic narrowing of the two-phase region on the R13B1 side of the phase diagram, especially at the highest temperature. This 'ibis beak' like structure is not the onset of an azeotrope, rather an indication of the nearness of the R13B1 critical point at 153 F (67 °C).

The equation of state was generated by first fitting the properties of the pure materials in the fashion refered to earlier. The value of the mixing parameter, f_{12}, was then adjusted to optimize the pressure correlation along the bubble curve. We elected to use only the pressure data and not include the volume data to find the mixing parameter because of the higher precision of the pressure measurement. The pressures are correlated to +/- 0.7 psia (5 kPa); the predicted volumes fall consistently at the high end of the uncertainty of the measured volumes.

upon the notion that Nature behaves in a well-ordered way and that, even when the scientist is unable to ascertain the connection between molecular structure and macroscopic properties from first principles, the apparent correlation between them can be used with certitude. The method of corresponding states is firmly rooted in molecular theory and the origin of the acentric factor, although itself an arbitrary construct, is understood from perturbation theory. These methods, far from producing quantitative information from 'nothing,' are then founded on physical principles and extensive correlation of data.

Let us now consider the state of the mixing rules for multicomponent systems. In a binary mixture, a molecule can have at least two kinds of interactions, with like and unlike species. Such a notion is appropriate in the dilute gas phase; in the liquid phase, the character of like and unlike interactions is profoundly affected by the molecular composition surrounding the pair. A modest effort to account for the surroundings are 'two-fluid' models for mixtures (Scott 1956).

In the simplest mixture models, the effective molecular parameters in the mixture are evaluated as follows:

$$a = \sum_{i=1}^{2} \sum_{j=1}^{2} x_i x_j a_{ij} \tag{3}$$

$$b = \sum_{i=i}^{2} \sum_{j=1}^{2} x_i x_j b_{ij} \tag{4}$$

When $i=j$, the values of a and b are those of the pure materials. The values of a_{12} and b_{12} can be obtained if the values of a and b are known for the mixture; however, the motivation of the mixing rules is to determine a_{12} and b_{12} without the assistance of measurements. The simplest approach is to use the van der Waals and Lorentz rules, for which

$$a_{12} = (a_{11} a_{22})^{1/2} , \tag{5}$$

$$b_{12} = (b_{11} + b_{22})/2 , \tag{6a}$$

or

$$b_{12} = (b_{11}^{1/3} + b_{22}^{1/3})^3/8 . \tag{6b}$$

(Unless the two molecular volumes differ by more than 42%, these two schemes for b_{12} will differ by less than 1% and will lead to less than 1/4% difference in the evaluation of b for the mixture.)

Often, these mixing rules are found not to be adequate. The value of a_{12} is typically altered by using the following prescription:

$$a_{12} = (1 - f_{12}) (a_{11} a_{22})^{1/2} \tag{7}$$

These mixing rules are completely empirical, especially the device represented by f_{12}. Let us consider the schemes for predicting this interaction parameter. For mixtures of the noble gases, Equation 8 gives one of the simplest estimates for the value of f_{12}:

$$1 - f_{12} = \frac{2(I_i I_j)^{1/2}}{I_i + I_j} \frac{2^6 \sigma_{ii}^3 \sigma_{jj}^3}{(\sigma_{ii} + \sigma_{jj})^6} \tag{8}$$

where $I_{i(\text{or } j)}$ is the ionization potential and σ_{ii} is the molecular diameter of species i (or j). This expression tries to compensate for the difference in the polarizability (or the ease with which the electron clouds are deformed) between the molecular species. Knobler (1978) has shown that even for so simple mixtures as He/Ne, He/Ar, He/Kr, and He/Xe that Equation 8 is far from adequate. For example, he shows that for He/Xe, the experimental value of $1-f_{12}$ is 0.611 and the predicted value is 0.824. Pesuit (1978) has compared at least half a dozen different semiempirical schemes of estimating f_{12} for many different kinds of mixtures. He is able to report the whole spectrum from success to failure for a large range of mixtures. The conclusion that one would draw from Knobler and Pesuit is that the methods for estimating f_{12} are not very satisfactory, that a method appropriate for one class of mixtures needn't be satisfactory for another.

the perfect gas heat capacities. Neilson and White (1959) have measured the enthalpy change associated with the complete evaporation of mixtures of R12/R22 over the entire composition range at -60.07 F (222.00 K). Their data, plotted in Figure 4a, are integral quantities because the composition of the liquid changed as the evaporation proceeded. The prediction of a closely related quantity, the enthalpy change associated with the complete vaporization of the liquid mixture at fixed composition to its vapor at the same fixed composition, is shown by the solid curve in Figure 4a. The agreement between these two closely related quantities is on the order of +/- 0.5 %; the equation of state predicts nearly quantitatively the curvature associated with the composition. By using these evaporation data, Neilson and White were also able to evaluate a quantity closely related to the enthalpy of mixing along the saturation line, H^E. The comparison of their calculated values and the predicted values are shown in Figure 4b. The equation of state overpredicts this quantity. One should note, however, that the quantities are not exactly the same and that the experimental value should underpredict slightly. The comparison between the two is encouraging indeed. That such intricate details about this mixture are accessible through so little information is a demonstration of the power and versatility of the perturbed hard sphere equation of state.

THE EFFECT OF NEARBY CRITICAL POINTS

Throughout the past few sections, we have compared a fluid mixture model based upon a hard-sphere reference fluid and the actual behavior of pure and mixed refrigerant materials. By using this model, the thermodynamic properties of these fluids, both pure and mixed, can be described by having only a modest set of experimental information. In making the comparisons, we have avoided critical points, one phenomenon that cannot be described quantitatively by this or any of the commonly used industrial equations of state.

First, let us note that this model has a critical point. Were we to use data far from the critical point (Sengers et al. 1981) to evaluate the parameters in the equation, we would find the following discepencies between the measured and predicted critical properties: first, the predicted and measured critical points would not coincide within experimental uncertainty; second, the predicted values of all the extensive properties — volumes, enthalpies, entropies, etc. — would differ from the measured values in fundamental ways; finally, the values of the thermodynamic response functions — heat capacities at both constant pressure and temperature, the isothermal compressibility, and the thermal expansion coefficient — would all diverge more strongly near the critical point than those respective properties predicted by the equation of state.

One is tempted to resolve these differences by forcing the equation of state to match the critical behavior. Such coercion does not represent an acceptable solution to what is a fundamental physical problem. Forcing the equation of state to match the critical behavior affects the temperature dependence of the molecular parameters, a and b; thus, states far from the critical density — and critical point — but near the critical temperature would 'sense' the critical point in a physically unrealistic way. The alteration of an equation of state to produce both proper near-critical and far-from-critical behavior is a major task (Woolley, 1983) and will not be discussed here. As long as one is not operating too near the critical point, a somewhat subjective prescription that depends upon the property being considered, 'classical' equations of state, such as the one discussed in this paper, can describe the properties of a fluid quite accurately.

There are advantages to using a function that can describe both liquid and vapor states, even if it cannot describe the critical region. The first is that separate schemes for liquids and vapors are not needed. The second is that mixing prescriptions, particularly for the liquid phase, that work well when both the components of the mixture are well below or above their critical points can collapse completely when one of the components is near its critical point, even when the mixture is an 'ordinary' liquid (Morrison 1985). Using a good equation of state will work so long as the fluid of interest is not near-critical. Depending upon the property, a 'classical' equation may even be adequate in the critical region.

A striking example of the effects of a nearby critical point can be seen in the measurements of the enthalpy of mixing of CO_2 and toluene (Morrison et al. 1985) shown in Figure 5. Were this an ideal mixture, all the data would fall on the line $H^E=0$. Indeed, were both these materials 'ordinary' liquids under the conditions of these experiments, one would expect nearly ideal behavior, at least on the scale of this figure. The details of this figure are discussed elsewhere. Similar kinds of behavior can be seen in the volumes of mixing (Eckert et al. 1983). These large departures from ideal mixing are inevitable whenever one of the components in the mixture is near-critical. Although none of the properties of the mixture may show

AZEOTROPES AND THE EQUILIBRIUM PROPERTIES OF R12/R22

In the previous section, we have examined the simplest kind of behavior one can expect from a mixture of two liquids, complete miscibility and the monotone variation of properties from one pure component to the other. In this section, we shall consider an example of the next most complex behavior case, azeotropy. Our motivation in this section is twofold, first, to discuss the situations when one can expect an azeotrope and second, to examine a refrigerant mixture for which there are calorimetric data.

Let us consider the situation when one would expect an azeotrope. An azeotrope is inevitable when the saturation curves of the two components cross in the p-T projection. Such a point of apparent intersection is called a 'Bancroft point' (Rowlinson and Swinton 1982b); the mixture R12/R152a, also known as R500, shows just such a behavior. In mixtures where there is a Bancroft point, the azeotrope can traverse the entire composition range; for R500 this behavior is intercepted by the solid phase and the critical locus (Pennington 1952). Since any kind of non-ideal behavior causes a deviation from the Raoult law prediction, the closer the vapor pressures of the two components, the more likely there will be an extremum in the T-x or p-x lines and, hence, an azeotrope. Closeness of vapor pressures is often associated with closeness of critical temperatures, since, with a few notable exceptions, the critical pressure of many materials are nearly the same, about 600 psia (4 MPa), and saturation lines are roughly parallel in a p-T projection. One can thus conclude that two materials with nearly the same critical temperature are likely to show azeotropic behavior. A sharp demarcation cannot be drawn, however; a certain critical temperature difference needn't guarantee the presence or absence of an azeotrope. That depends upon the molecular character of the components in the mixture.

The mixture R12/R22, also known as R501, has an azeotrope that emerges from the pure R22 axis of the phase diagram at approximately 116 F (320 K) and moves into the mixture region as the temperature is lowered until, at -40 F (233 K), the azeotropic composition is approximately 10 mol percent R12 (Spauschus 1962). The variation of the azeotropic composition with temperature is not unusual; however, the amount by which it can vary with temperature will be different from one mixture to another. The azeotrope in R12/R22 is a positive azeotrope (Rowlinson and Swinton 1982b); that is, the boiling curve will have a maximum pressure when measured at constant temperature or, conversely, a minimum temperature when measured at constant pressure. This kind of azeotrope is what one would typically expect from refrigerant mixtures. The opposite kind of behavior is typically encountered when the two components interact strongly, such as the hydrogen bonding encountered in chloroform/acetone (Karr et al. 1951).

The mixture R12/R22 shows azeotropic behavior over a range of temperatures and compositions as shown in Figure 3. The azeotropic point is typically found by locating an extremum in the bubble point curve; at such an extremum, the second law of thermodynamics requires the liquid and vapor phases to have the same composition and the dew and bubble lines to be tangent (Bett et al. 1975). Because of the flatness of these lines around an azeotrope, the uncertainty in the composition is typically large. The data of Eiseman (1957), for example, determine the azeotrope only to within 5 mole percent as shown by the error bar in Figure 3.

The equation of state parameters for pure R12 and R22 were determined by using data from the ASHRAE tables (1981). The procedure for evaluating a and b was the same as described in the previous section for the refrigerants R13B1 and R152a; values for the molecular parameters are given in Appendix B. Figures 2a and 2b show the comparison between the properties consistent with the equation of state and the properties in the tables. The mixing parameter was determined by fitting the bubble point predicted by the equation of state to the constant pressure boiling temperatures measured by Eiseman (1957) over the full range of compositions. The value of the mixing parameter was slightly composition dependent; a value averaged over the entire composition range (f_{12} = 0.0406 +/- .0088) was used.

The first test of the equation of state for the R12/R22 mixture is the comparison of its prediction of the temperature dependence of the azeotropic composition. The solid curve in Figure 3 shows that the prediction falls within the experimental measurements of the azeotrope. As we have noted previously, there is considerable uncertainty in those points. The dashed line in the figure is the locus suggested by Spaschus (1962) from measurements he made on a grid of composition-temperature conditions. Our prediction, which arises from data at a single pressure, nearly coincides with Spauschus's experimental locus.

The equation of state contains enough information to evaluate enthalpies as long as the temperature is fixed; for differences in enthalpy due to temperature changes, one also needs

critical behavior, one must always keep nearby critical points in mind because the properties of mixtures change rapidly near them and because neglect of such effects can lead to serious errors in mass and energy balance calculations.

DISCUSSION

We have shown that an equation of state founded on a realistic physical model, the hard sphere fluid, can correlate both liquid and vapor data without the need for adding a huge number of correction terms to the equation. This has been shown both with the pure refrigerants, R12, R22, R13B1, and R152a, and in the mixture R13B1/R152a. For the pure materials, the saturation properties were represented to within a few tenths of a percent, within the precision for many of these properties. Not until the temperature approached the critical point did deviations exceed this range. For the mixture, the pressures were represented to +/- 0.7 psia (5 kPa) and the molar volumes from 0.0 to + 0.5 % of the measured value. One should note that volume, because of its sensitivity to microscopic geometric details, is the most difficult of the properties of a mixture to predict.

We have also shown that the perturbed hard sphere model can be used with confidence to predict properties that may not have been measured. This was shown by the ability to predict the temperature dependence of the azeotropic composition in the mixture R12/R22. This prediction arose from the correlation of the pure components and a single bubble point curve. We have also shown that the equation of state was able to predict the detailed behavior of the enthalpy of vaporization as a function of composition.

Finally, we examined the state of theory of mixing rules. We have argued that the schemes used classically work marginally well even for mixtures of the noble gases and that methods to expand the mixing rules to more complex molecules are not dependable. We suggest that the area of mixing rules is one ripe for research and that efforts to predict the mixing parameters from first principles are showing promise. We advise, however, that the most certain values of the mixing parameters will always be those originating from experimental data.

NOMENCLATURE

$a(a_{ij})$ = equation of state parameter associated with intermolecular attraction (between species i and j)

$a'(a'')$ = first (and second) derivative of a with respect to temperature

$A(A^{pg})$ = molar Helmholtz free energy (of a perfect gas reference fluid)

$b(b_i)$ = equation of state parameter associated with the hard core of a molecule (of species i)

$b'(b'')$ = the first (and second) temperature derivative of b

B = second virial coefficient

$C_v(C_p)$ = molar heat capacity at constant volume (pressure)

$E(E^{pg})$ = molar internal energy (of a perfect gas reference fluid)

f_{ij} = an empirical function to compensate for the real behavior in a mixture of species i and j

$G(G^{pg})$ = molar Gibbs free energy (of a perfect gas reference fluid)

$H(H^{pg})$ = molar enthalpy (of a perfect gas reference fluid)

I = ionization potential

p = pressure

$p*$ = pressure of a perfect gas reference fluid equal to the saturation pressure of the pure component at the temperature T

R	= gas constant
$S(S^{pg})$	= molar entropy (of a perfect gas reference fluid)
T	= thermodynamic temperature
v	= molar volume
x_i	= mole fraction of component i
y	= function defined in equation 1
β	= b/4
$\beta'(\beta'')$	= first (and second) temperature derivatives of β
β_i	= $b_i/4$
μ_i	= chemical potential of species i
σ	= molecular diameter

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$$G(p^*, T\ v) = G^{pg}(p^*,T) + RT \ln\left(\frac{RT}{p^*v}\right) - \frac{a}{b} \ln\left(\frac{v+b}{v}\right) + \frac{RT\beta}{(v-\beta)^3}(8v^2 - 9v\beta + 3\beta^2) - \frac{a}{v+b}$$

$$\mu(p^*, T, x_i; v) = G(p^*, T, x_i, v) + (1-x_i)\left(\frac{\partial G}{\partial x_i}\right)_{T,p}$$

$$= \mu^{pg}(p^*, T, x_i) + RT \ln\left(\frac{RT}{p^*v}\right) + \frac{RT\beta(4v-3\beta)}{(v-\beta)^2} + \frac{RT\beta_i(4v^2-2v\beta)}{(v-\beta)^3} + \frac{ab_i}{b^2}\ln\left(\frac{v+b}{v}\right)$$

$$- \frac{ab_i}{b(v+b)} + \frac{2x_ia_i + 2x_ja_{ij}}{b}\ln\left(\frac{v}{v+b}\right)$$

Note: the above expression for chemical potential applies only to a binary mixture.

$$S(v,T,x) = S^{pg}(v,T,x) + \frac{a'b - ab'}{b^2}\ln\left(\frac{v+b}{v}\right) + \frac{ab'}{b(v+b)} - \frac{R\beta(4v-3\beta)}{(v-\beta)^2} - \frac{RT\beta'(4v^2-2v\beta)}{(v-\beta)^3}$$

$$E(v,T) = E^{pg}(v,T) + \frac{a'bT - ab'T - ab}{b^2}\ln\left(\frac{v+b}{v}\right) + \frac{ab'T}{b(v+b)} - \frac{RT^2\beta'(4v^2-2v\beta)}{(v-\beta)^3}$$

$$H(p,T;v) = H^{pg}(T) + \frac{ab'T - ab'T - ab}{b^2}\ln\left(\frac{v+b}{b}\right) + \frac{ab'T - ab}{b(v+b)} + \frac{RT(4v^2-2v\beta)(\beta - \beta'T)}{(v-\beta)^3}$$

$$C_v(v,T) = C_v^{pg}(T) + \frac{6RT^2\beta'^2(v\beta - 2v^2)}{(v-\beta)^4} + \frac{2RTv((\beta''T + 2\beta')(\beta - 2v) + \beta'^2T)}{(v-\beta)^3} - \frac{Tab'}{b(v+b)^2}$$

$$+ \frac{T(ab''b + 2a'b'b + 2ab'^2)}{b^2(v+b)} - \frac{(a''b^2T - 2a'b'bT + 2ab'^2T - ab''bT)}{b^3}\ln\left(\frac{v+b}{v}\right)$$

$$C_p = C_v - T\left(\frac{\partial p}{\partial T}\right)^2_{v,x} \Big/ \left(\frac{\partial p}{\partial v}\right)_{T,x}$$

APPENDIX B

TEMPERATURE DEPENDENCE OF EQUATION OF STATE PARAMETERS

$$a(kJ\ m^3/(kg\ mol)^2) = a_0 \exp(a_1 T + a_2 T^2)$$

$$b(m^3/kg\ mol) = b_0 + b_1 T + b_2 T^2$$

	R12	R13B1	R22	R152a
a_0	3524.12	2728.10	2514.59	2254.37
a_1	-2.77230×10^{-3}	-2.79791×10^{-3}	-2.38706×10^{-3}	-5.87778×10^{-4}
a_2	-6.73180×10^{-7}	-1.50848×10^{-6}	-1.83653×10^{-6}	-4.37432×10^{-6}
b_0	0.153755	0.139949	0.113681	0.116521
b_1	-1.84195×10^{-4}	-1.82428×10^{-4}	-1.16201×10^{-4}	-9.04883×10^{-5}
b_2	-5.03644×10^{-8}	-7.75898×10^{-8}	-9.24562×10^{-8}	-1.14563×10^{-7}

Mixture interaction parameter

R13B1/R152a $\quad\quad f_{12} = 0.0902$
R12/R22 $\quad\quad\quad\quad f_{12} = 0.0406$

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ACKNOWLEDGEMENTS

APPENDIX A

THERMODYNAMIC FUNCTIONS ARISING FROM THE PERTURBED CARNAHAN-STARLING EQUATION OF STATE

$$\frac{pv}{RT} = \frac{1 + y + y^2 - y^3}{(1 - y)^3} - \frac{a}{RT(v + b)}$$

$$y = b/4v$$

$$A(v,T) = A^{pg}(v, T) - \frac{a}{b} \ln \left(\frac{v + b}{v} \right) + \frac{4RT\beta}{(v - \beta)} + \frac{RT\beta^2}{(v - \beta)^2}$$
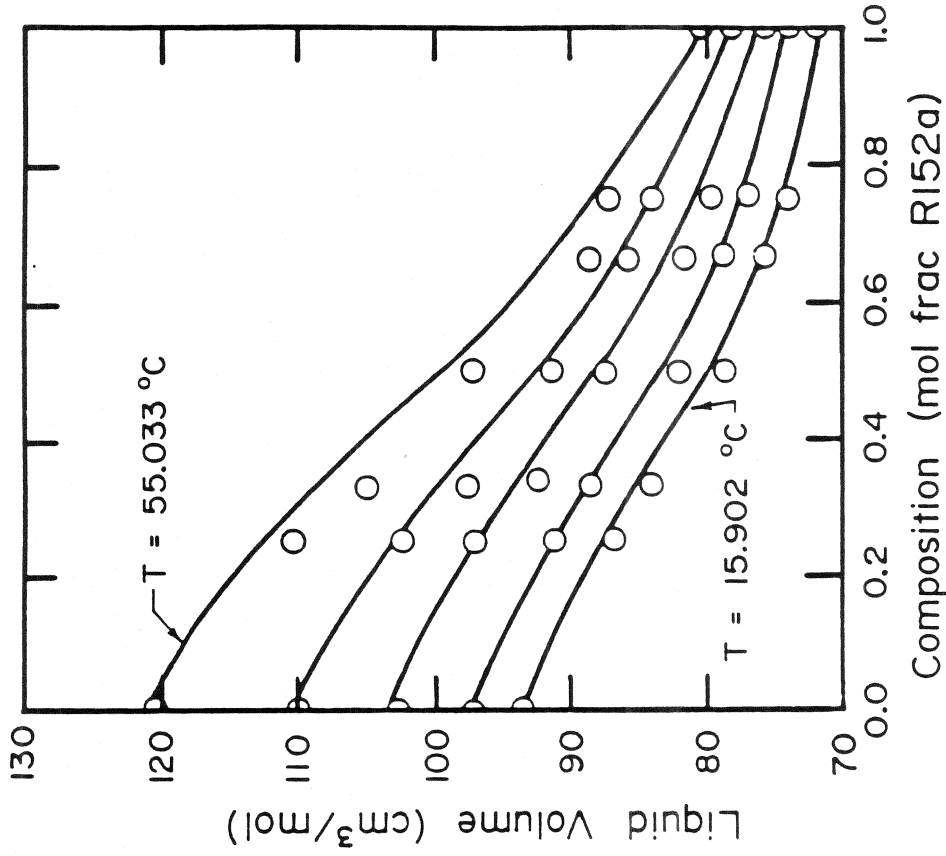
$$\beta = b/4$$

Figure 1b. *The saturated liquid volumes for the mixture R13B1/R152a plotted against the mole fraction of R152a. The open circles are the measured points, and the lines, the predicted values. The temperatures are identical to those of Figure 1a*
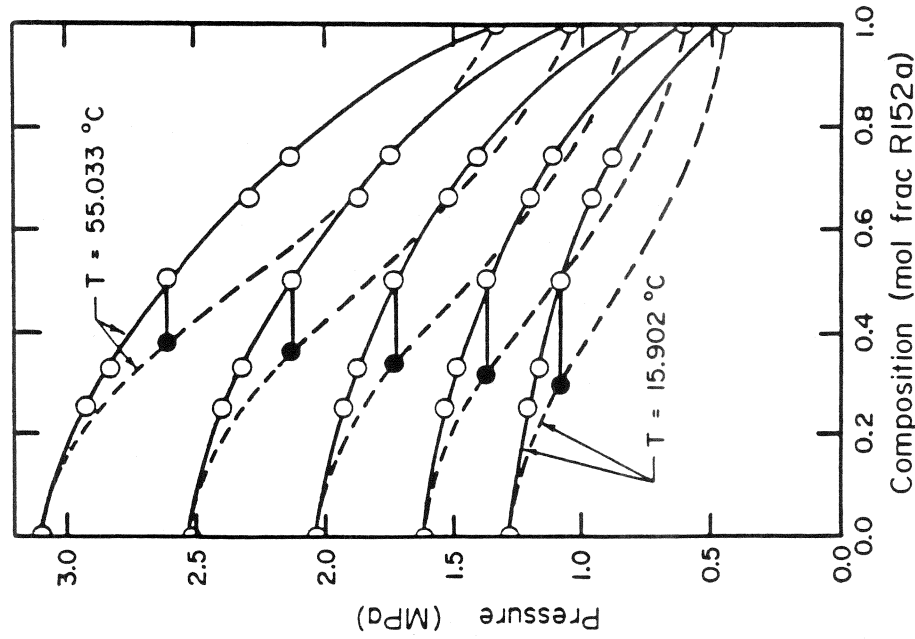

Figure 1a. *The saturation pressures for the mixture R13B1/R152a plotted against the mole fraction of R152a. The open circles, O, are experimental bubble points, the closed circles, ●, dew points. The solid and dashed curves are the predicted bubble and dew curves respectively beginning at the lowest pressure and temperature 15.902°C, and increasing in temperature to 25.323°C, 35.323°C, 45.134°C, and 55.033°C*
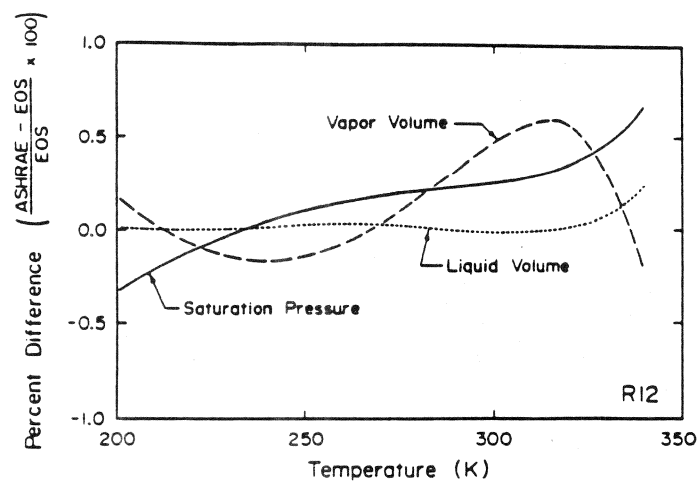
Figure 2a. *The correlation between tabulated (ASHRAE, 1981) and equation of state data for R12: (˙ ˙ ˙), liquid volumes; (- - -), vapor volumes, and (___), vapor pressures*
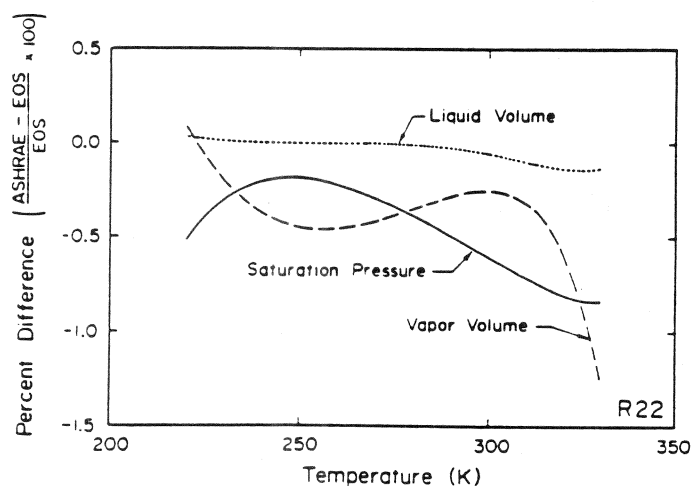

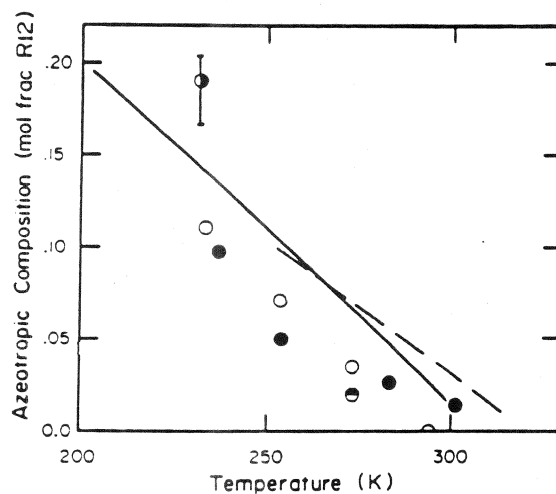Figure 2b. *The correlation between tabulated and equation of state data for R22*

Figure 3. *The variation between the azeotropic composition for R12/R22; (——), this work; (---), Spauschus (1962); ◑,Eiseman (1957); O, Loffler and Kaltetechnik, v. 12, p. 256 (1960); ◓, Pennington, World Refrig. v. 8, p. 151 (1957); ●, Madinabeitia, thesis, "The Effect of Pressures and Temperature on Azeotropic Composition in the R12 and R22 Binary System," University of Delaware (June 1960)*
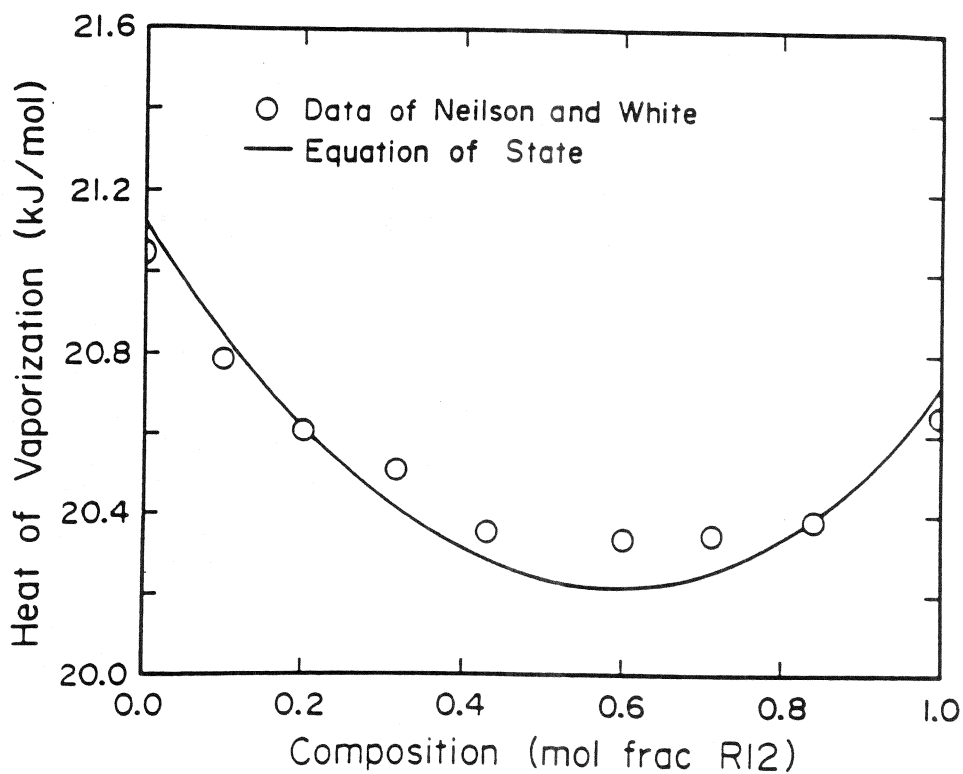
Figure 4a. *The heat of complete vaporization at 222.00 K for the mixture R12/R22. The points are data by Neilson and White (1959); the solid line, the values predicted by the equation of state*
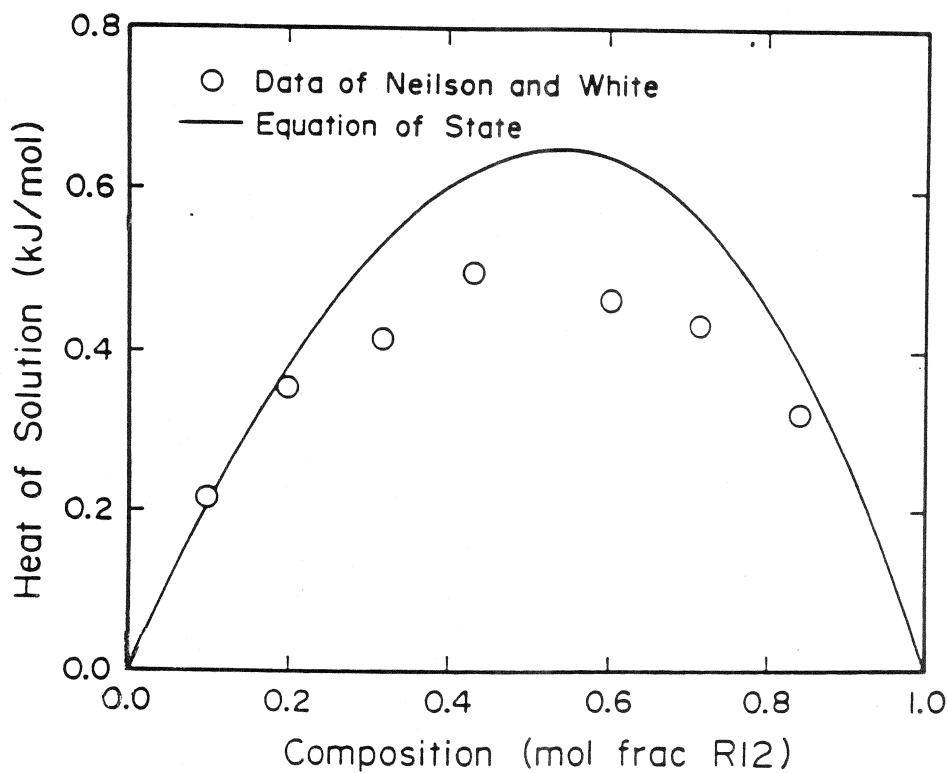

Figure 4b. *The heat of mixing at 222.00 K for the mixture R12/R22 at saturation. The points are data (Neilson and White); and solid curve, this work*
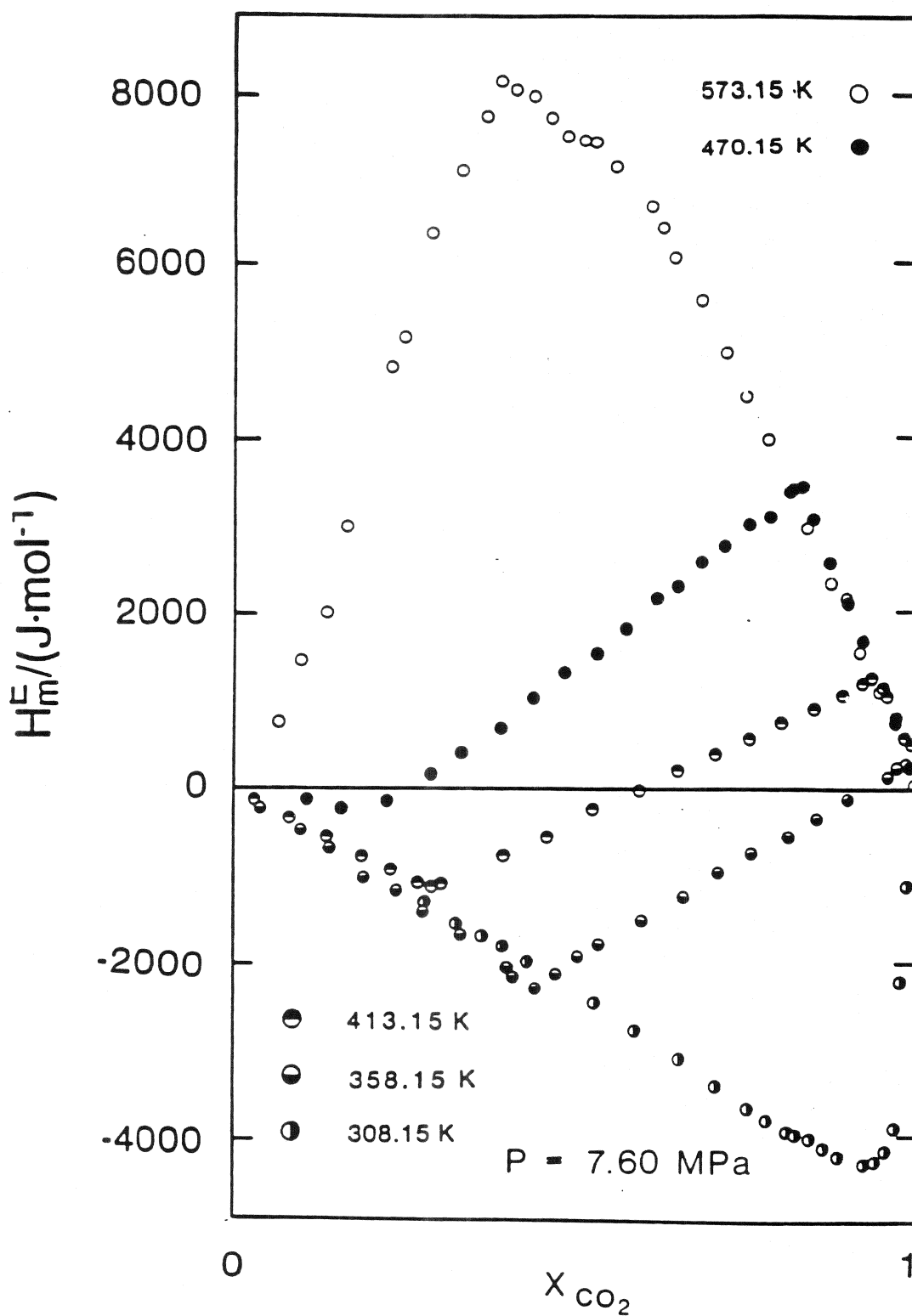
Figure 5. The heat of mixing for the mixture CO_2/toluene (C_7H_8) at the critical pressure of CO_2 and at various temperatures (Morrison et al., 1985)